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(19)(CA) **CANADIAN PATENT** (12)

(54) 7-Aminoazolo[1,5-A] Pyrimidines, and Fungicides Containing These

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1985/09/17

(57) 11 Claims

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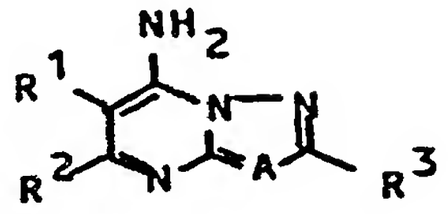
ABSTRACT OF THE DISCLOSURE:

Disclosed are novel, specific 7-aminoazolo-[1,5-a] pyrimidines of the formula:



where R^1 is aryloxyalkoxyalkyl, alkoxyalkoxyalkyl, alkoxyalkoxyalkoxyalkyl or dialkylaminoalkyl, in which the aryl moiety is unsubstituted or monosubstituted or polysubstituted by straight-chain or branched alkyl, aryl, alkoxy, aryloxy, halogen, arylalkyl, arylalkoxy, dialkylamino or alkylarylamino, R^2 and R^3 are each hydrogen or alkyl and A is =N-, =CH-, =CBr- or =CCl-. These compounds have a fungicidal action superior to the known compounds of the same family, in particular in the case of Oomycetes, thereby making them useful as fungicides.

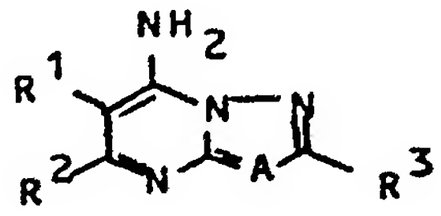
D

The present invention relates to novel, specific 7-aminoazolo[1,5-a]pyrimidines, and to fungicides containing them.

It is known that 7-aminoazolo[1,5-a]pyrimidines, in particular 7-amino-6-phenyl-5-methyl-1,2,4-triazolo[1,5-a]pyrimidine, possess pharmacological properties (U.S. Patent 2,553,500).

It is also known that 7-aminoazolo[1,5-a]pyrimidines, in particular 7-amino-6-(4-tert-butoxybut-1-yl)-2,5-di-methylpyrazolo[1,5-a]pyraimidine, can be used as a fungicidal active ingredient (European Patent 141,317). However, their fungicidal action is not adequate.

It has now been found that novel, specific 7-aminoazolo-[1,5-a]pyrimidines of the formula:



where R^1 is aryloxyalkoxyalkyl, alkoxyalkoxyalkyl, alkoxyalkoxyalkoxyalkyl or dialkylaminoalkyl, in which the aryl moiety is unsubstituted or monosubstituted or polysubstituted by straight-chain or branched alkyl, aryl, alkoxy, aryloxy, halogen, arylalkyl, arylalkoxy, dialkylamino or alkylarylamino, R^2 and R^3 are each hydrogen or alkyl and A is =N-, =CH-, =CBr- or =CCl-, are superior to the known compounds in their fungicidal action, in particular in the case of Oomycetes.

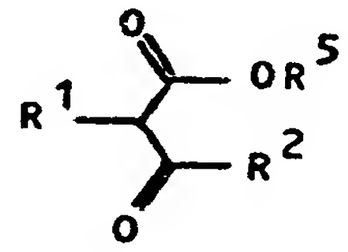
More specifically, R^1 is phenyl- or naphthyloxy-C_2-C_6-alkoxy-C_2-C_6-alkyl where the alkoxy and alkyl group have a straight-chain or are branched and the phenyl or naphthyl group can be monosubstittued or polysubstituted by

straight-chain or branched C_1-C_{10}-alkyl, C_1-C_{10}-alkoxy, aryl, aryloxy, fluorine, chlorine, bromine, aryl-C_1-C_4-alkyl, aryl-C_1-C_4-alkoxy, di-C_1-C_{10} alkylamino or C_1-C_{10}-alkylarylamino; aryl being phenyl or 1- or 2-naphthyl. R^1 may furthermore be C_1-C_{10}-alkoxy-C_2-C_6 alkoxy-C_2-C_6-alkyl, C_1-C_{10}-alkoxy-C_2-C_6-alkoxy-C_2-C_6-alkoxy-C_2-C_6-alkyl, where the alkoxy and alkyl group once again have a straight-chain or are branched, or di-C_1-C_{10}-alkyl-amino-C_2-C_6-alkyl.

R^2 and R^3 are each hydrogen or C_1-C_4-alkyl, methyl being preferred.

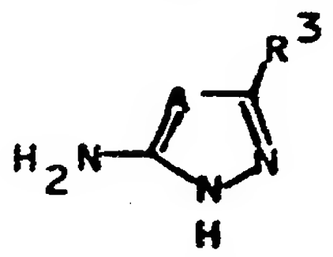
C

7-aminoazolo[1,5-a]pyrimidines of the formula I are obtained, for example, by a method in which an appropriately substituted β-ketoester of the formula II



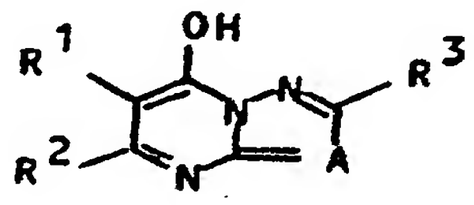
II,

where R^5 is lower alkyl, is reacted with an appropriate aminoazole of the formula III



III,

to give a condensate of the formula V



V,

and this is halogenated at the hydroxyl group and reacted with ammonia (process A).

The preparation of the β-ketoesters (II) can be carried out as described in Organic Synthesis Coll., vol. 1, page 248, or in German Laid-Open Application DOS3,227,388. The reaction (condensation) with the aminoazoles (III) can be carried out in the presence or absence of solvents. Suitable solvents are, in particular, alcohols, such as ethanol, propanols, butanols, glycols or glycol monoethers,

C

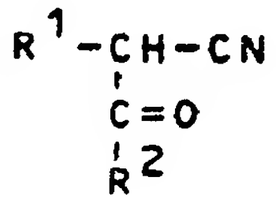
diethylene glycols and their monoethers, amides, such as dimethylformamide, diethylformamide, dibutylformamide or N,N-dimethylacetamide, lower alkanoic acids, such as formic acid, acetic acid or propionic acid, and mixtures of these solvents with water. The reaction temperature is in general from 50 to 300°C, preferably from 50 to 150°C, when a solvent is employed.

The condensates are generally obtained in pure form and are washed (for example with the same solvent or with water) and then dried, after which they are halogenated with, for example, a phosphorus halide at the reflux temperature, preferably at from 50 to 150°C in excess phosphorus oxytrichloride. A stoichiometric amount or an excess of a base, eg. N,N-dimethylaniline, may be added. The excess phosphorus oxytrichloride is evaporated, after which the mixture is treated with icewater, with or without the addition of a water-immiscible solvent, and, if necessary, the base is removed by extraction with hydrochloric acid.

The chlorination product finally obtained is generally very pure and is therefore most advantageously reacted directly with ammonia to give the novel 7-aminoazolo[1,5-a]pyrimidines. This is preferably carried out using ammonia in an excess of from 1 to 10 moles per mole of the pyrimidine, under superatmospheric pressure (up to 100 bar) above about 100°C and, if necessary, in a solvent.

The novel 7-aminoazolo[1,5-a]pyrimidines are generally crystalline compounds obtained directly in very pure form.

The 7-aminoazolo[1,5-a]pyrimidines (I) may also be prepared by a method in which an appropriately substituted α-acylnitrile of the formula



IV,

is reacted with an aminoazole of the formula (III) (process B), this process too being carried out in the presence or absence of a solvent. The solvents and the process conditions are substantially similar to those recommended for process A. Process B gives the novel 7-aminoazolo[1,5-a]pyrimidines directly; they are isolated as crystalline, generally very pure compounds, if necessary after evaporation of the solvent or dilution with water. When lower alkanoic acids (fatty acids) are used as solvents, it is advantageous to neutralize residual acid, if necessary after partial evaporation of the excess.

Some of the substituted α-acylnitriles (VI) required for the preparation of the 7-amino-azolo[1,5-a]pyrimidines are known; individual unknown nitriles of this type may be prepared by a known method from nitriles possessing α hydrogen and carboxylic esters using strong bases, eg. alkali metal hydrides, alkali metal amides or metalalkylenes (J. Amer. Chem. Soc. 73, (1951), page 3766).

Preparation example

Process A

7-amino-5-methyl-6-[2-(2-methoxy-1-ethoxy)-prop-1-yl]-1,2,4-triazolo[1,5-a]pyrimidine (corresponds to Example no. 97 in the Table)

a) 7-hydroxy-5-methyl-6-[2-(2-methoxy-1-ethoxy)-prop-1-yl]-1,2,4-triazolo[1,5-a]pyrimidine

43.6 g of 86 percent strength (corresponding to 37.5 g of 100 percent pure material, 161 millimoles) of methyl 2-[2-(2-methoxy-1-ethoxy)-prop-1-yl]-acetoacetate are reacted with 16.8 g (200 millimoles) of 3-amino-1H-1,2,4-triazole in 300 ml of propionic acid for 24 hours at 60°C under a protective gas. The mixture is cooled, stirred into icewater and then neutralized with 2 N NaOH, and any precipitate is filtered off. The aqueous phase is extracted four times with methylene chloride, and the extracts are dried and evaporated down. The resulting oil is triturated with diethyl ether and

the crystals which separate out are filtered off under suction and dried. Yield: 17.5 g (41% of theory); mp. 127 - 128°C. The infrared spectrum shows that the substance is predominantly in the form of the 7-oxo-4H tautomer.

b) 7-Chloro-5-methyl-6-[2-(2-methoxy-1-ethoxy)-prop-1-yl]-1,2,4-triazolo[1,5-a]pyrimidine

16.0 g (56.2 millimoles) of the intermediate obtained as described in method a) are boiled for 20 hours in 300 ml of phosphorus oxytrichloride. Excess phosphorus oxytrichloride is then distilled off. The residue is treated first with water and then with aqueous sodium bicarbonate solution. Extraction is carried out several times with methylene chloride and the extract is extracted several times with water. Drying and evaporating down the extract gives 12.5 g (78%, based on the intermediate) of an oil, which is used for the next stage c) without further purification.

c) Active ingredient, corresponding to Example 97 in the Table

460 millimoles of gaseous ammonia are allowed to act on a solution of 12.0 g (42.1 millimoles) of the chlorine compound from b) in 200 ml of dry 1,4-dioxane in an autoclave under an initial pressure of 100 bar at 130°C for 60 hours. The autoclave is cooled and let down, after which the mixture is taken up in water and extracted several times with methylene chloride. The extract is dried, the solvent is distilled off and the residue is triturated with n-pentane to give 5.0 g (45%, based on the chlorine compound) of a crystalline material of melting point 143-144°C.

Preparation example

Process B

7-amino-5-methyl-6-{3-[2-(2,4,6-trichlorophenoxy)-1-ethoxy]-prop-1-yl}-1,2,4-triazolo[1,5-a]pyrimidine (Example no. 8 in the Table)

a) 2-acetyl-5-[2-(2,4,6-trichlorophenoxy)-1-ethoxy]-valeronitrile

245 g (760 millimoles) of 5-[2-(2,4,6-trichlorophenoxy)-1-ethoxy]-valeronitrile are dissolved in 1 l of dried tetrahydrofuran and the solution is cooled to -68°C under a protective gas. 572 ml of a 1.5 molar solution of n-butyllithium in n-hexane (corresponding to 858 millimoles of n-butyllithium) are added dropwise in the course of 3 hours, and the mixture is stirred for a further 3 hours at -60°C. 74.0 ml (66.7 g; 758 millimoles) of dry ethyl acetate, dissolved in 200 ml of dry tetrahydrofuran, are then slowly added. The mixture is left for a further 3 hours at -60°C and allowed to reach room temperature overnight. Excess butyllithium is destroyed by carefully adding water and the pH is brought to four by adding 2 N hydrochloric acid. Thereafter, the organic phase is separated off, washed with water, dried and evaporated down. The residue which remains comprises 267 g (crude yield 73%) of a yellow oil, which can be used directly for reaction b).

b) Active ingredient, corresponding to Example 8 in the Table

The total amount (732 mmoles) of the α-acetylnitrile prepared as described above and 61.5 g (731 mmoles) of 3-amino-1H-1,2,4-triazole in 1.0 l of propionic acid are kept at the boil for 24 hours, after which the mixture is allowed to cool and is filtered, and the filtrate is evaporated down. The residue is taken up in methylene chloride, and the solution is washed several times with water until the aqueous phase is neutral, and is then dried and evaporated down. 166 g of (53%, based on the nitrile) of a crystalline material of melting point 193-194°C result.

Preparation example

Process B

7-amino-5-methyl-6-{2-[N-(3,5,5-trimethylhex-1-yl)-N-methylamino]-1-ethyl}-1,2,4-triazolo[1,5-a]pyrimidine (Example no. 125)

a) 2-acetyl-4-[N-(3,5,5-trimethylhex-1-yl)-N-methylamino]-butyronitrile

As described above, 31.3 g (139.5 mmoles) of 4-[N-(3,5,5-trimethylhex-1-yl)-N-methylamino]-butyronitrile in 300 ml of dry tetrahydrofuran are first reacted with 103 ml of 1.5 M n-butyllithium solution (154 mmoles) and the product is then reacted with 13.7 ml (12.4 g; 141 mmoles) of dry ethyl acetate in 50 ml of tetrahydrofuran at -68°C. In working up the mixture, the pH is brought to 6 with 2 N hydrochloric acid. The solvent is evaporated off to give 33.0 g (crude yield 88%) of an oil, which is used directly for the subsequent product.

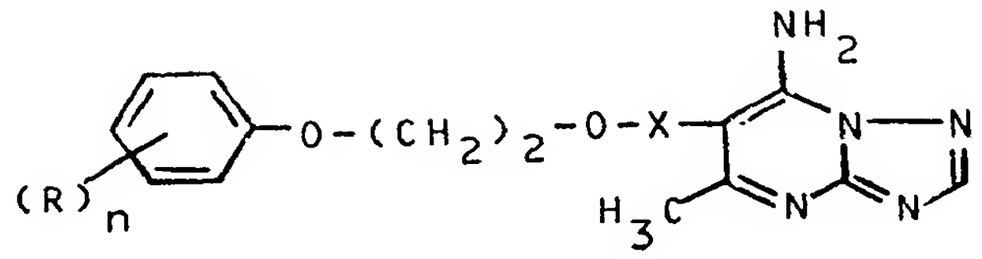
b) Active ingredient, corresponding to Example 125

The total amount (124 mmoles) of the resulting nitrile is reacted with 10.4 g (124 mmoles) of 3-amino-1H-1,2,4-triazole in 300 ml of boiling propionic acid for 18 hours. The solvent is removed, the residue is triturated with n-pentane, the mixture is filtered under suction, the residue is taken up in methylene chloride and the solution is filtered over a short column of silica gel, with the addition of 5 percent by volume of methanol. The eluate is extracted by shaking with aqueous sodium carbonate solution, dried and evaporated down. 13.0 g (32%, based on the nitrile) of a solid of melting point of 109-110°C remain.

The active ingredients characterized more exactly (melting point, state of aggregation, etc.) in the tables below are prepared by the stated processes (A or B). Those compounds which are not characterized can readily be obtained by appropriately changing the starting materials and adapting the methods of preparation; because

of their structural similarity, they are expected to have a similar action.

Table 1 a

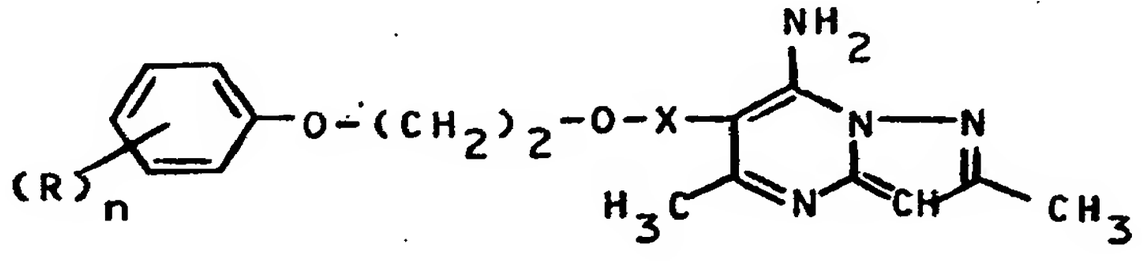


No.	$(R)_n$	-X-	M.p. (°C)
1	H	$-(CH_2)_2-$	
2	H	$-CH(CH_3)CH_2-$	
3	H	$-(CH_2)_3-$	157-158
4	H	$-(CH_2)_4-$	
5	H	$-(CH_2)_5-$	
6	2,4,6-Cl_3	$-(CH_2)_2-$	
7	2,4,6-Cl_3	$-CH(CH_3)CH_2-$	
8	2,4,6-Cl_3	$-(CH_2)_3-$	
9	2,4,6-Cl_3	$-(CH_2)_4-$	
10	2,4,6-Cl_3	$-(CH_2)_5-$	
11	2-Cl	$-(CH_2)_2-$	
12	2-Cl	$-CH(CH_3)CH_2-$	
13	2-Cl	$-(CH_2)_3-$	
14	2-Cl	$-(CH_2)_4-$	
15	2-Cl	$-(CH_2)_5-$	
16	4-Cl	$-(CH_2)_2-$	
17	4-Cl	$-CH(CH_3)CH_2-$	
18	4-Cl	$-(CH_2)_3-$	
19	4-Cl	$-(CH_2)_4-$	
20	4-Cl	$-(CH_2)_5-$	
21	3-Cl	$-(CH_2)_2-$	
22	3-Cl	$-CH(CH_3)CH_2-$	
23	3-Cl	$-(CH_2)_3-$	135-137
24	3-Cl	$-(CH_2)_4-$	
25	3-Cl	$-(CH_2)_5-$	
26	2-Br	$-(CH_2)_2-$	
27	2-Br	$-CH(CH_3)CH_2-$	
28	2-Br	$-(CH_2)_3-$	161-163
29	2-Br	$-(CH_2)_4-$	
30	2-Br	$-(CH_2)_5-$	
31	4-Br	$-(CH_2)_2-$	
32	4-Br	$-CH(CH_3)CH_2-$	
33	4-Br	$-(CH_2)_3-$	

No.	$(R)_n$	-X-	M.p. (°C)
34	4-Br	$-(CH_2)_4-$	
35	4-Br	$-(CH_2)_5-$	
36	2-CH_3	$-(CH_2)_2-$	
37	2-CH_3	$-CH(CH_3)CH_2-$	
38	2-CH_3	$-(CH_2)_3-$	164-166
39	2-CH_3	$-(CH_2)_4-$	
40	2-CH_3	$-(CH_2)_5-$	220 (decomposition)
41	3-CH_3	$-(CH_2)_2-$	
42	3-CH_3	$-CH(CH_3)CH_2-$	
43	3-CH_3	$-(CH_2)_3-$	147-149
44	3-CH_3	$-(CH_2)_4-$	
45	3-CH_3	$-(CH_2)_5-$	
46	4-CH_3	$-(CH_2)_2-$	
47	4-CH_3	$-CH(CH_3)CH_2-$	
48	4-CH_3	$-(CH_2)_3-$	155-158
49	4-CH_3	$-(CH_2)_4-$	
50	4-CH_3	$-(CH_2)_5-$	
51	2,4,6-$(CH_3)_3$	$-(CH_2)_2-$	
52	2,4,6-$(CH_3)_3$	$-CH(CH_3)CH_2-$	
53	2,4,6-$(CH_3)_3$	$-(CH_2)_3-$	190-191
54	2,4,6-$(CH_3)_3$	$-(CH_2)_4-$	
55	2,4,6-$(CH_3)_3$	$-(CH_2)_5-$	157-160
56	tert.-C_4H_9-CH_2-$C(CH_3)_2$	$-(CH_2)_2-$	
57	tert.-C_4H_9-CH_2-$C(CH_3)_2$	$-CH(CH_3)CH_2-$	
58	tert.-C_4H_9-CH_2-$C(CH_3)_2$	$-(CH_2)_3-$	
59	tert.-C_4H_9-CH_2-$C(CH_3)_2$	$-(CH_2)_4-$	
60	tert.-C_4H_9-CH_2-$C(CH_3)_2$	$-(CH_2)_5-$	149-151
61	4-Cl-2-CH_3	$-(CH_2)_3-$	144-145
62	2-(i-C_3H_7)	$-(CH_2)_3-$	
63	2-(sec-C_4H_9)	$-(CH_2)_3-$	118-120
64	2-(sec-C_4H_9)	$-(CH_2)_5-$	154-156
65	4-C_6H_5	$-(CH_2)_3-$	176-179
66	4-C_6H_5	$-(CH_2)_5-$	172-174
67	4-H_5C_2O	$-(CH_2)_2-$	162-163
68	4-H_5C_2O	$-CH(CH_3)CH_2-$	158-160
69	4-H_5C_2O	$-(CH_2)_3-$	
70	4-H_5C_2O	$-(CH_2)_4-$	
71	4-H_5C_2O	$-(CH_2)_5-$	
72	4-H_5C_6O	$-(CH_2)_2-$	
73	4-H_5C_6O	$-CH(CH_3)CH_2-$	

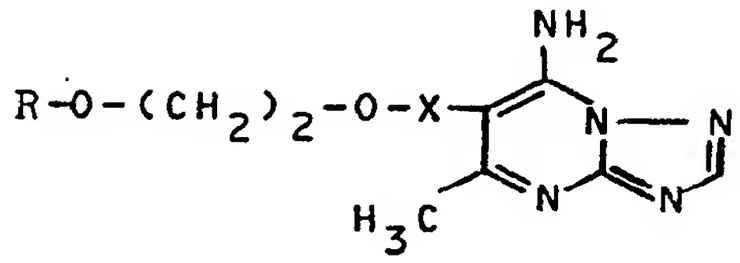
No.	$(R)_n$	-X-	M.p. (°C)
74	4-H_5C_6O	-$(CH_2)_3$-	156-158
75	4-H_5C_6O	-$(CH_2)_4$-	
76	4-H_5C_6O	-$(CH_2)_5$-	
77	2-(n-C_4H_9)O	-$(CH_2)_3$-	133-135
78	2-(n-C_4H_9)O	-$(CH_2)_4$-	
79	2-(n-C_4H_9)O	-$(CH_2)_5$-	
80	3-(n-C_4H_9)O	-$(CH_2)_3$-	
81	3-(n-C_4H_9)O	-$(CH_2)_4$-	
82	3-(n-C_4H_9)O	-$(CH_2)_5$-	
83	4-(n-C_4H_9)O	-$(CH_2)_3$-	
84	4-(n-C_4H_9)O	-$(CH_2)_4$-	
85	4-(n-C_4H_9)O	-$(CH_2)_5$-	
86	2-(H_5C_6-CH_2)O	-$(CH_2)_3$-	
87	2-(H_5C_6-CH_2)O	-$(CH_2)_5$-	
88	3-(H_5C_6-CH_2)O	-$(CH_2)_3$-	
89	3-(H_5C_6-CH_2)O	-$(CH_2)_5$-	
90	4-(H_5C_6-CH_2)O	-$(CH_2)_3$-	
91	4-(H_5C_6-CH_2)O	-$(CH_2)_5$-	
92	3-(H_5C_2)N	-$(CH_2)_3$-	
93	3-(H_5C_2)N	-$(CH_2)_5$-	

Table 1 b



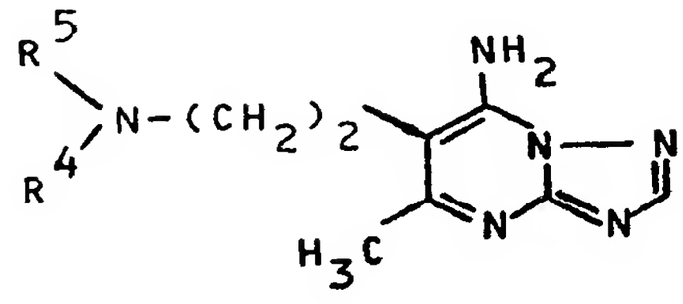
No.	$(R)_n$	-X-	M.p. (°C)
94	t-C_4H_9-CH_2-$C(CH_3)_2$-	-$(CH_2)_3$-	60
95	t-C_4H_9-CH_2-$C(CH_3)_2$-	-$(CH_2)_5$-	(oil)

Table 2



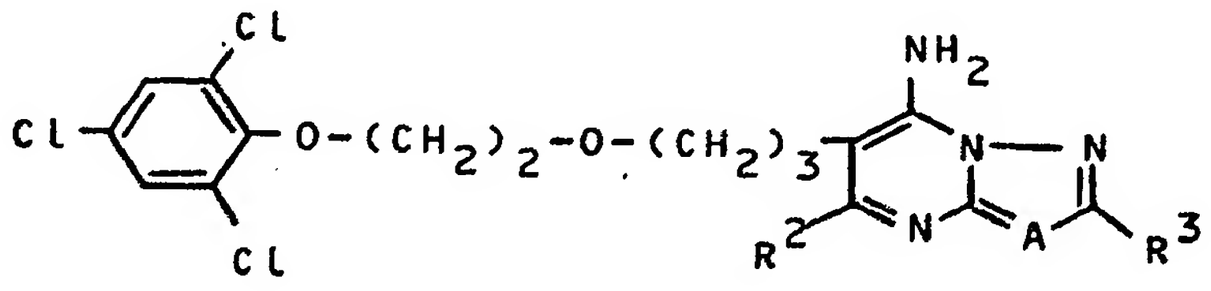
No.	R	-X-	M.p. (°C)
96	CH_3	$-(CH_2)_2-$	
97	CH_3	$-CH(CH_3)CH_2-$	142-144
98	CH_3	$-(CH_2)_3-$	
99	CH_3	$-(CH_2)_4-$	
100	CH_3	$-(CH_2)_5-$	
101	$n-C_4H_9$	$-(CH_2)_2-$	
102	$n-C_4H_9$	$-CH(CH_3)CH_2-$	
103	$n-C_4H_9$	$-(CH_2)_3-$	
104	$n-C_4H_9$	$-(CH_2)_4-$	
105	$n-C_4H_9$	$-(CH_2)_5-$	
106	2-ethylhexyl	$-(CH_2)_2-$	
107	2-ethylhexyl	-CH(Me)CH_2-	
108	2-ethylhexyl	$-(CH_2)_3-$	
109	2-ethylhexyl	$-(CH_2)_4-$	
110	2-ethylhexyl	$-(CH_2)_5-$	
111	3,5,5-trimethylhexyl	$-(CH_2)_2-$	
112	3,5,5-trimethylhexyl	$-CH(CH_3)CH_2-$	
113	3,5,5-trimethylhexyl	$-(CH_2)_3-$	
114	3,5,5-trimethylhexyl	$-(CH_2)_4-$	
115	3,5,5-trimethylhexyl	$-(CH_2)_5-$	
116	$n-H_9C_4-O-(CH_2)_3-$	$-(CH_2)_2-$	
117	$n-H_9C_4-O-(CH_2)_3-$	$-CH(CH_3)CH_2-$	resin
118	$n-H_9C_4-O-(CH_2)_3-$	$-(CH_2)_3-$	
119	$n-H_9C_4-O-(CH_2)_3-$	$-(CH_2)_4-$	
120	$n-H_9C_4-O-(CH_2)_3-$	$-(CH_2)_5-$	
121	$n-H_9C_4-O-(CH_2)_2-$	$-CH(CH_3)CH_2-$	
122	$CH_2O(CH_2)_2-$ $H_5C_2-\overset{*}{C}H-n-C_4H_9$	$-CH(CH_3)CH_2-$	
123	$(CH_2)_2O(CH_2)_2-$ $H_3C-\overset{*}{C}H-CH_2-t-C_4H_9$	$-CH(CH_3)CH_2-$	

Table 3



No.	R^5	R^4	M.p. (°C)
124	$n\text{-}C_6H_{13}$-	$n\text{-}C_6H_{13}$-	139-140
125	3,5,5-trimethylhexyl-	CH_3-	109-110

Table 4



No.	R^2	R^3	A	M.p. (°C)
126	H	H	N	
127	CH_3	CH_3	N	
128	CH_3	CH_3	CH	
129	CH_3	CH_3	C-Br	

The novel active ingredients have a strong fungitoxic action on phytopathogenic fungi, especially from the Phycomycetes class. The novel compounds are therefore suitable for combatting Phytophthora infestans in tomatoes and potatoes, Phytophthora parasitica in strawberries, Phytophthora cactorum in apples, Pseudoperonospora cubensis in cucumbers, Pseudoperonospora humuli in hops, Peronospora destructor in onions, Peronospora sparsa in roses, Peronospora tabacina in tobacco, Plasmopara viticola in grapes, Plasmopara halstedii in sunflowers, Sclerospora macrospora in Indian corn, Bremia lactucae in lettuce, Mucor mucedo in fruit, Rhizopus nigricans in beets, Erysiphe graminis in cereals, Uncinula necator in grapes, Podosphaera leucotricha in apples, Sphaerotheca fuliginea in roses, and Erysiphe cichoriacearum in cucumbers.

The active ingredients are well tolerated by plants. Some of the active ingredients have curative properties, i.e., the agents may also be applied after the plants have been infected by the pathogen, and success is still ensured.

The fungicidal agents contain from 0.1 to 95, and preferably from 0.5 to 90, wt.% of active ingredient. The application rates depend on the type of effect desired, and range from 0.1 to 5 kg/ha.

The active ingredients may also be mixed and applied together with other active ingredients, e.g., herbicides, insecticides, growth regulators and other fungicides, or with fertilizers. When they are mixed with other fungicides, the spectrum of fungicidal action is often increased, i.e., the fungicidal action of the combination is greater than the sum of the actions of the individual components.

Examples of fungicides which may be combined with the novel compounds are:

sulfur

dithiocarbamates and derivatives thereof, such as

ferric dimethyldithiocarbamate

zinc dimethyldithiocarbamate
zinc ethylenebisthiocarbamate
manganese ethylenebisdithiocarbamate
manganese zinc ethylenediaminebisdithiocarbamate
tetramethylthiuram disulfides
ammonia complex of zinc N,N'-ethylenebisdithiocarbamate
ammonia complex of zinc N,N-propylenebisdithiocarbamate
zinc N,N'-propylenebisdithiocarbamate and
N,N-polypropylenebis(thiocarbamyl) disulfide
nitro derivatives, such as
dinitro (1-methylheptyl)-phenyl crotonate
2-sec-butyl-4,6-dinitrophenyl-3,3-dimethylacrylate
2-sec-butyl-4,6-dinitrophenyl isopropylcarbonate and
diisopropyl 5-nitroisophthalate

heterocyclic substances, such as
2-heptadecylimidazol-2-yl acetate
2,4-dichloro-6-(o-chloroanilino)-s-triazine
O,O-diethyl phthalimidophosphonothionate
5-amino-1-[bis-(dimethylamino)-phosphinyl]-3-phenyl-1,2,4-
-triazole
2,3-dicyano-1,4-dithiaanthraquinone
2-thio-1,3-dithio-[4,5-b]-quinoxaline
methyl 1-(butylcarbamoyl)-2-benzimidazole carbamate
2-methoxycarbonylaminobenzimidazole
2-[furyl-(2)]-benzimidazole
2-[thiazolyl-(4)]-benzimidazole
N-(1,1,2,2-tetrachloroethylthio)-tetrahydrophthalimide
N-trichloromethylphthalimide
N-dichlorofluoromethylthio-N+,N+-dimethyl-N-phenyl-
-sulfuric acid diamide
5-ethoxy-3-trichloromethyl-1,2,3-thiadiazole
2-thiocyanomethylthiobenzthiazole
1,4-dichloro-2,5-dimethoxybenzole
4-(2-chlorophenylhydrazono)-3-methyl-5-isoxazolone
2-thiopyridine 1-oxide
8-hydroxyquinoline and its copper salt

2,3-dihydro-5-carboxanilido-6-methyl-1,4-oxathiin
2,3-dihydro-5-carboxanilido-6-methyl-1,4-oxathiin 4,4-dioxide
2-methyl-5,6-dihydro-4-H-pyran-3-carboxanilide
2-methylfuran-3-carboxanilide
2,5-dimethylfuran-3-carboxanilide
2,4,5-trimethylfuran-3-carboxanilide
2,5-dimethyl-N-cyclohexylfuran-3-carboxamide
N-cyclohexyl-N-methoxy-2,5-dimethyl-furan-3-carboxamide
2-methylbenzanilide
2-iodobenzanilide
N-formyl-N-morpholine-2,2,2-trichloroethylacetal
piperazine-1,4-diylbis-(1-(2,2,2-trichloroethyl)-formamide
1-(3,4-dichloroanilino)-1-formylamino-2,2,2-trichlorethane
2,6-dimethyl-N-tridecyl-morpholine and its salts
2,6-dimethyl-N-cyclododecyl-morpholine and its salts
N-[3-(p-tert.-butylphenyl)-2-methylpropyl]-cis-2,6-dimethylmorpholine
N-[3-(p-tert.-butylphenyl)-2-methylpropyl]-piperidine
1-[2-(2,4-dichlorophenyl)-4-ethyl-1,3-dioxolan-2-yl-ethyl]--1-H-1,2,4-triazole
1-[2-(2,4-dichlorophenyl)-4-n-propyl-1,3-dioxolan-2-yl--ethyl]-1-H-1,2,4-triazole
N-(n-propyl)-N-(2,4,6-trichlorophenoxyethyl)-N+-imidazolyl-urea
1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)--butan-2-one
1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)-butan-2-ol
alpha-(2-chlorophenyl)-alpha-(4-chlorophenyl)-5-pyrimidine-methanol
5-butyl-2-dimethylamino-4-hydroxy-6-methylpyrimidine
bis-(p-chlorophenyl)-3-pyridinemethanol
1,2-bis-(3-ethoxycarbonyl-2-thioureido)-benzene
1,2-bis-(3-methoxycarbonyl-2-thioureido)-benzene
2-cyano-N-(ethylaminocarbonyl)-2-(methoximino)-acetamide

and various fungicides, such as
dodecylguanidine acetate
3-[2-(3,5-dimethyl-2-oxycyclohexyl)-2-hydroxyethyl]-glutaramide
hexachlorobenzene
DL-methyl-N-(2,6-dimethylphenyl)-N-fur-2-yl alanate
methyl DL-N-(2,6-dimethylphenyl)-N-(2'-methoxyacetyl)--alanate
N-(2,6-dimethylphenyl)-N-chloroacetyl-DL-2-aminobutyrolactone
5-methyl-5-vinyl-3-(3,5-dichlorophenyl)-2,4-dioxo-1,3-oxazolidine
3-(3,5-dichlorophenyl)-5-methyl-5-methoxymethyl-1,3-oxazolidine-2,4-dione
3-(3,5-dichlorophenyl)-1-isopropylcarbamoylhydantoin
N-(3,5-dichlorophenyl)-1,2-dimethyl-cyclopropane-1,2-dicarboximide

The novel active ingredients may be applied for instance in the form of directly sprayable solutions, powders, suspensions (including high-percentage aqueous, oily or other suspensions), dispersions, emulsions, oil dispersions, pastes, dusts, broadcasting agents, or granules by spraying, atomizing, dusting, broadcasting or watering. The forms of application depend entirely on the purpose for which the agents are being used, but they must ensure as fine a distribution of the novel active ingredients as possible.

For the preparation of solutions, emulsions, pastes and oil dispersions to be used direct or after emulsification in water, mineral oil fractions of medium to high boiling point, such as kerosene or diesel oil, further coal-tar oils, and oils of vegetable or animal origin, aliphatic, cyclic and aromatic hydrocarbons such as benzene, toluene, xylene, paraffin, tetrahydronaphthalene, alkylated naphthalenes and their derivatives such as methanol, ethanol, propanol, butanol, chloroform, carbon tetrachloride, cyclohexanol, cyclohexanone, chlorobenzene,

isophorone, etc., and strongly polar solvents such as dimethylformamide, dimethyl sulfoxide, N-methylpyrrolidone, water, etc. are suitable.

Aqueous formulations may be prepared from emulsion concentrates, pastes, oil dispersions or wettable powders by adding water. To prepare emulsions, pastes and oil dispersions the ingredients as such or dissolved in an oil or solvent may be homogenized in water by means of wetting or dispersing agents, adherents or emulsifiers. Concentrates which are suitable for dilution with water may be prepared from active ingredient, wetting agent, adherent, emulsifying or dispersing agent and possibly solvent or oil.

Examples of surfactants are: alkali metal, alkaline earth metal and ammonium salts of ligninsulfonic acid, naphthalenesulfonic acids, phenolsulfonic acids, alkylaryl sulfonates, alkyl sulfates, and alkyl sulfonates, alkali metal and alkaline earth metal salts of dibutylnaphthalenesulfonic acid, lauryl ether sulfate, fatty alcohol sulfates, alkali metal and alkaline earth metal salts of fatty acids, salts of sulfated hexadecanols, heptadecanols, and octadecanols, salts of sulfated fatty alcohol glycol ethers, condensation products of sulfonated naphthalene and naphthalene derivatives with formaldehyde, condensation products of naphthalene or naphthalenesulfonic acids with phenol and formaldehyde, polyoxyethylene octylphenol ethers, ethoxylated isooctylphenol, ethoxylated octylphenol and ethoxylated nonylphenol, alkylphenol polyglycol ethers, tributylphenyl polyglycol ethers, alkylaryl polyether alcohols, isotridecyl alcohol, fatty alcohol ethylene oxide condensates, ethoxylated castor oil, polyoxyethylene alkyl ethers, ethoxylated polyoxypropylene, lauryl alcohol polyglycol ether acetal, sorbitol esters, lignin, sulfite waste liquors and methyl cellulose.

Powders, dusts and broadcasting agents may be prepared by mixing or grinding the active ingredients with a solid carrier.

Granules, e.g., coated, impregnated or homogeneous granules, may be prepared by bonding the active ingredients to solid carriers. Examples of solid carriers are mineral earths such as silicic acid, silica gels, silicates, talc, kaolin, attapulgus clay, limestone, lime, chalk, bole, loess, clay, dolomite, diatomaceous earth, calcium sulfate, magnesium sulfate, magnesium oxide, ground plastics, fertilizers such as ammonium sulfate, ammonium phosphate, ammonium nitrate, and ureas, and vegetable products such as grain flours, bark meal, wood meal, and nutshell meal, cellulosic powders, etc.

Examples of formulations are given below.

I. 90 parts by weight of the compound of Example 3 is mixed with 100 parts by weight of N-methyl-alpha-pyrrolidone. A mixture is obtained which is suitable for application in the form of very fine drops.

II. 20 parts by weight of the compound of Example 8 is dissolved in a mixture consisting of 80 parts by weight of xylene, 10 parts by weight of the adduct of 8 to 10 moles of ethylene oxide and 1 mole of oleic acid-N-monoethanolamide, 5 parts by weight of the calcium salt of dodecylbenzenesulfonic acid, and 5 parts by weight of the adduct of 40 moles of ethylene oxide and 1 mole of castor oil. By pouring the solution into water and uniformly distributing it therein, an aqueous dispersion is obtained.

III. 20 parts by weight of the compound of Example 23 is dissolved in a mixture consisting of 30 parts by weight of cyclohexanone, 30 parts by weight of isobutanol, and 20 parts by weight of the adduct of 40 moles of ethylene oxide and 1 mole of castor oil. By pouring the solution into water and finely distributing it therein, an aqueous dispersion is obtained.

IV. 20 parts by weight of the compound of Example 38 is dissolved in a mixture consisting of 25 parts by weight of cyclohexanol, 65 parts by weight of a mineral oil fraction having a boiling point between 210° and 280°C, and

10 parts by weight of the adduct of 40 moles of ethylene oxide and 1 mole of castor oil. By pouring the solution into water and uniformly distributing it therein, an aqueous dispersion is obtained.

V. 20 parts by weight of the compound of Example 43 is well mixed with 3 parts by weight of the sodium salt of diisobutylnaphthalene-alpha-sulfonic acid, 17 parts by weight of the sodium salt of a lignin-sulfonic acid obtained from a sulfite waste liquor, and 60 parts by weight of powdered silica gel, and triturated in a hammer mill. By uniformly distributing the mixture in water, a spray liquor is obtained.

VI. 5 parts by weight of the compound of Example 94 is intimately mixed with 95 parts by weight of particulate kaolin. A dust is obtained containing 5% by weight of the active ingredient.

VII. 30 parts by weight of the compound of Example 117 is intimately mixed with a mixture consisting of 92 parts by weight of powdered silica gel and 8 parts by weight of paraffin oil which has been sprayed onto the surface of this silica gel. A formulation of the active ingredient is obtained having good adherence.

VIII. 40 parts by weight of the compound of Example 124 is intimately mixed with 30 parts of the sodium salt of a phenolsulfonic acid-urea-formaldehyde condensate, 2 parts of silica gel and 48 parts of water to give a stable aqueous dispersion.

IX. 20 parts of the compound of Example 23 is intimately mixed with 2 parts of the calcium salt of dodecylbenzenesulfonic acid, 8 parts of a fatty alcohol polyglycol ether, 2 parts of the sodium salt of a phenol-sulfonic acid-urea-formaldehyde condensate and 68 parts of a paraffinic mineral oil. A stable oily dispersion is obtained.

The following experiments demonstrate the biological action of the novel compounds. The prior art compounds 7-amino-6-phenyl-5-methyl-[1,2,4]-triazole-[1,5-a]-pyrimi-

dine (A) (U.S. 2,553,500) and 7-amino-6-(4-tert-butoxy)--5-methyl-2-methylpyrazolo-[1,5-a]-pyrimidine (B) (EP 141,317) were used for comparison purposes.

Experiment 1

Action on Plasmopara viticola

Leaves of potted vines of the Müller-Thurgau variety were sprayed with aqueous suspensions containing (dry basis) 80% of active ingredient and 20% of emulsifier. To assess the duraction of action, the plants were set up, after the sprayed-on layer had dried, for 10 days in the greenhouse. Then the leaves were infected with a zoospore suspension of Plasmopara viticola. The plants were first placed for 16 hours in a water-vapor saturated chamber at 24°C and then in a greenhouse for 8 days at from 20° to 30°C. To accelerate and intensify the sporangiophore discharge, the plants were then again placed in the moist chamber for 16 hours. The extent of fungus attack was then assessed on the undersides of the leaves.

The results of the experiment show that for instance compounds nos. 3, 8, 23, 38, 43, 94, 117 and 124, applied as 0.05% liquors, have a better fungicidal action (e.g., 97%) then comparative compounds A and B (e.g., 60%).

Experiment 2

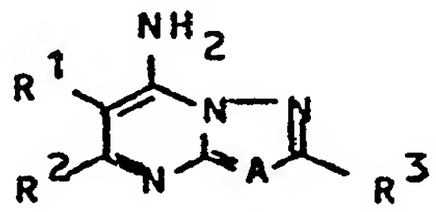
Action on Phytophthora infestans in tomatoes

Leaves of potted tomatoes of the "Große Fleischtomate" variety were sprayed with aqueous liquors containing (dry basis) 80% of active ingredient and 20% of emulsifier. After the sprayed-on layer had dried, the leaves were infected with a zoospore suspension of Phytophthora infestans. The plants were then placed for 5 days in a water vapor-saturated chamber kept at 16° to 18°C. After this period, the disease had spread on the untreated control plants to such an extent that the fungicidal action of the compounds was able to be assessed.

The results of this experiment show that compounds 8, 63 and 124, applied for instance as 0.025% liquors, have a better fungicial action (e.g., 97%) than prior art active ingredient B (0%).

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A 7-aminoazolo[1,5-a]pyrimidine of the formula:



where R^1 is phenyl- or naphthyloxy-C_2-C_6-alkoxy-C_2-C_6-alkyl where the alkoxy and alkyl group have a straight-chain or are branched and the phenyl or naphthyl group can be monosubstituted or polysubstituted by straight-chain or branched C_1-C_{10}-alkyl, C_1-C_{10}-alkoxy, aryl, aryloxy, fluorine, chlorine, bromine, aryl-C_1-C_4-alkyl, aryl-C_1-C_4-alkoxy, di-C_1-C_{10} alkylamino or C_1-C_{10}-alkylarylamino, aryl being phenyl or 1- or 2-naphthyl, or R^1 is C_1-C_{10}-alkoxy-C_2-C_6-alkoxy-C_2-C_6-alkyl, C_1-C_{10}-alkoxy-C_2-C_6-alkoxy-C_2-C_6-alkoxy-C_2-C_6-alkyl, where the alkoxy and alkyl group have a straight-chain or are branched, or di-C_1-C_{10}-alkyl-amino-C_2-C_6-alkyl;

R^2 and R^3 are each hydrogen or C_1-C_4-alkyl, and

A is =N-, =CH-, =CBr or =CCl.

2. A process for combatting fungi, wherein the fungi or the materials, plants soil or seed to be protected against fungus attack are treated with a fungicidally effective amount of a compound as set forth in claim 1.

3. A fungicidal composition comprising a suitable diluent or carrier and a fungicidally effective amount of a

compound as set forth in claim 1.

4. Amino-5-methyl-6-[2-(2-methoxy-1-ethoxy)-prop-1-yl]-1,2,4-triazolo[1,5a]-pyrimidine.

5. 7-Amino-5-methyl-6-{3-[2-(2,4,6-trichlorophenoxy)-1-ethoxy]-prop-1-yl }-1,2,4-triazolo[1,5a] pyrimidine.

6. 7-Amino-5-methyl-6-{3-[2-(phenoxy)-1-ethoxy]-prop-1-yl}-1,2,4-triazolo[1,5a]-pyrimidine.

7. 7-Amino-5-methyl-6-{2-[N,N-dihexylamino]-1-ethyl}-,2,4-triazolo[1,5a]pyrimidine.

8. A process for combatting fungi, wherein the fungi or the materials, plants soil or seed to be protected against fungus attack are treated with a fungicidally effective amount of a compound as claimed in claim 4 or 5.

9. A process for combatting fungi, wherein the fungi or the materials, plants, soil or seed to be protected against fungus attack are treated with a fungicidally effective amount of a compound as claimed in claim 6 or 7.

10. A fungicidal composition comprising a suitable diluent or carrier and a fungicidally effective amount a compound as claimed in claim 4 or 5.

11. A fungicidal composition comprising a suitable diluent or carrier and a fungicidally effective amount of a compound as claimed in claim 6 or 7.

C

*

SUBSTITUTE

REMPLACEMENT

SECTION is not Present

Cette Section est Absente